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WITNESS my hand this
Eleventh day of October 2000

LEANNE MYNOTT
<u>TEAM LEADER EXAMINATION</u>
<u>SUPPORT AND SALES</u>

CERTIFIED COPY OF PRIORITY DOCUMENT

AUSTRALIA

Patents Act 1990

Silverbrook Research Pty Ltd

PROVISIONAL SPECIFICATION

Invention Title:

Infrared-absorbing dyes

The invention is described in the following statement:

FIELD OF THE INVENTION

The present invention relates to compounds that are suitable for use as dyes. In particular, the present invention relates to compounds that are suitable for use as infrared dyes, to compositions containing these compounds, including colour light-sensitive material, and to processes for their use as infrared absorbers. The present invention has particular application to infrared printing inks.

BACKGROUND

Recently there has been renewed interest in "innovative" or "functional" dyes. One area of interest is that of optical recording technology where gallium aluminium arsenide (GaAlAs) and indium phosphide (InP) diode lasers are widely used as a light source. Since dyes absorbing in the near infrared (near-IR) region (i.e., beyond about 700 nanometers in wavelength and less than about 2000 nanometers in wavelength are required and the oscillation wavelengths fall in the near-infrared region, they are suitable candidates for use as infrared dyes.

Infrared dyes have applications in many areas. For example, infrared dyes are important in the optical data storage field, particular in the DRAW (Direct Reading After Writing) and WORM (Write Once, Read Many) disk, which is used for recording. Currently, indolinocyanine dyes, triphenylmethane dyes, naphthalocyanine dyes and indonanaphthalo-metal complex dyes are commercially available for use as organic colorants in DRAW disks. Cyanine dyes can only be used if additives improve the lightfastness.

Another application of infrared dyes is in thermal writing displays. In this application, heat is provided by a laser beam or heat impulse current. The most common type of infrared dyes used in this application are the cyanine dyes, which are known as laser dyes for infrared lasing.

Infrared dyes are also used as photoreceptors in laser printing. Some infrared-absorbing dyes are used in laser filters. They also find application in infrared photography and even have application in medicine, for example, in photodynamic therapy.

The compounds of the present invention will now be described in the context of printing inks and the like, but it will be understood by the skilled

reader that the compounds described hereunder may be used in other applications, for example, those set out above.

Fast, error-free data entry is important in current communication technology. Automatic reading of digital information in printed, digital and analog form is particularly important. An example of this technology is the use of printed bar codes that are scannable. In many applications of this technology, the bar codes are printed with an inks that are visible to the unaided eye. There are, however, applications (eg security coding) that require the barcode or other intelligible marking to be printed with an ink that invisible to the unaided eye but which can be detected under UV light or infrared light (IR).

For instance, U.S. Pat. No. 5,093,147 describes a method exploiting the process of fluorescence in which a dye is excited by ultra-violet (UV), visible or near-IR radiation and fluorescent light emitted by the dye material is detected. This reference describes a jet printing process used to apply a compatible liquid or viscous substance containing an organic laser dye that is poorly absorptive of radiation in the visible wavelength range of about 400 nm to about 700 nm, and is highly absorptive of radiation in the near-IR wavelength range of about 750 nm to about 900 nm. The dye fluoresces at longer wavelengths in the IR in response to radiation excitation in the near-IR range.

Another example is described in U.S. Pat. No. US Pat No. 5,460,646 (Lazzouni et al) which describes the use of a colorant which is silicon (IV) 2,3-naphthalocyanine bis($(R_1)(R_2)(R_3)$-silyloxide) wherein R_1, R_2, and R_3 are selected from the group consisting of an alkyl group, at least one aliphatic cyclic ring, and at least one aromatic ring.

The infrared absorbing dyes Squarylium and Croconium dyes have been extensively described in the literature (see for example, T. P. Simard, J. H. Yu, J. M. Zebrowski-Young, N. F. Haley and M. R. Detty, *J. Org. Chem.* **65** 2236 (2000), and J. Fabian, *Chem. Rev.* **92** 1197 (1992)). These prior art compounds have a central squarylium or croconium moiety connected to traditional electron donors. These donors act to donate an electron to the central squarylium or croconium moieties. However, these particular dyes do not absorb at a high enough wavelength and/or also absorb too strongly in the visible spectrum.

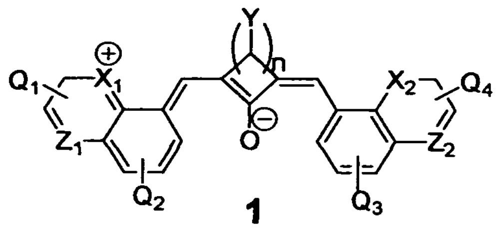
SUMMARY OF THE INVENTION

Conventional croconium and squarylium dyes have high wavelength absorption peaks, typically from 700 to 900 nanometers. The croconate dyes of Simard et al (supra) actually extend up to 1081 nanometers. However, the ratio of near infrared absorption, that is absorption from 700 to less than about 2000 nm in wavelength, to visible absorption for the croconate dyes is not sufficient. We have found that an improvement of this ratio can be achieved by combining two bridged diarylpolymethine type dyes with a squarylium, a croconium or derivative thereof whereby the bridged diarylpolymethine dyes are connected at either the 3, 4, 5 or 6 position to the central squarylium or croconium moiety or derivatives thereof. The diarylpolymethine dyes are in themselves a dye that absorbs strongly in the visible parts of the spectrum. We have found that a specific combination of these dyes to the central squarylium and croconium moieties or derivatives thereof gives a compound that absorbs strongly in the near infrared and poorly in the visible parts of the spectrum.

Accordingly, in a first aspect, the present invention provides an infrared dye, characterised in that the dye comprises two bridged diarylpolymethine type dyes or derivatives thereof connected together at either the 3, 4, 5 or 6 position by a central moiety such that the two dyes are located on each side of the central moiety, wherein the infrared dye absorbs strongly in the near infrared region of the spectrum but poorly in the visible region of the spectrum.

Preferably, the central moiety is selected from the group consisting of squarylium, croconium, methinologs thereof and derivatives thereof.

In a particularly preferred form, the present invention provides an infrared dye of formula 1, 2, 3 or 4 as set out hereunder:



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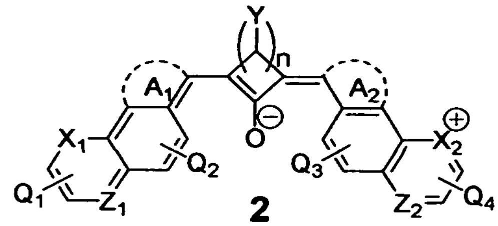

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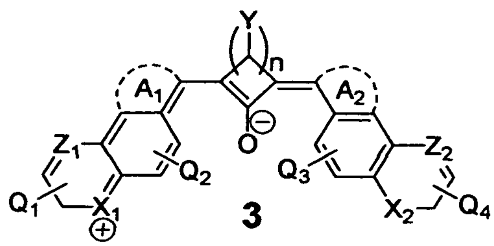

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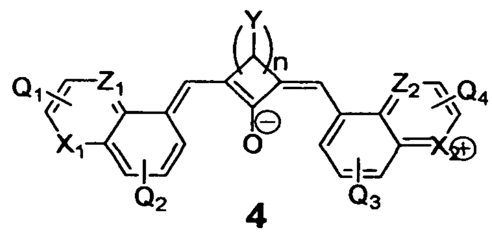

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wherein A_1 and A_2, taken individually, is/are absent or selected from the group consisting of a 5-membered polyene ring containing 0, 1 or 2 substituents that are selected from the group R;

X_1 and X_2 are individually selected from the group consisting of oxygen, sulfur, selenium, tellurium, CR_1R_2, NR_1, SiR_1R_2, GeR_1R_2, PR_1 where R_1 and R_2, which may the same or different, are selected from the group R;

Z_1 and Z_2 are individually selected from CR_3 or N where R_3 is selected from the group R;

Q_1, Q_2, Q_3 and Q_4 are individually selected from the group consisting of R_4, a fused 6-membered aromatic ring optionally substituted with 1 to 4 substituents individually selected from R_5, and fused polyaromatic rings optionally substituted with one or more substituents selected from R_6 wherein R_4,, R_5 and R_6 are individually selected from the group R ;

R is the group consisting of hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted aralkyl group, a halide atom, a hydroxy group, a substituted or unsubstituted amine group, a substituted or unsubstituted alkoxy group; and

n is 1 or 2 or 3.

The dyes of the present invention may be synthesized in a similar manner to the squarylium and croconium dyes described in Simard et al and the references cited therein. A typical reaction scheme for these particular dyes starts with the methylated bridged diarylpolymethine type dyes or derivatives

thereof. The methyl group can be directed to either the 3, 4, 5 or 6 positions by standard techniques. The salt of the dehydrogenated bridged diarylpolymethine dye is combined with a squarylium moiety to give the 2,2'-bridged diarylpolymethine squarylium dyes and their lesser annulated forms **1** to **4**.

In a second aspect, the present invention provides an infrared printing ink comprising a colorant, wherein the colorant is a dye in accordance with the first aspect of the invention.

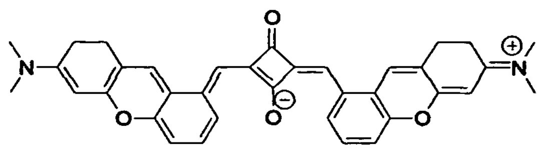
The infrared printing ink of the second of the invention may be suitable for use as an ink jet printing ink, offset printing ink, etc. The printing ink of the present invention may include other components conventionally incorporated into inks, for example, carriers, solvents and additives that affect properties of the ink, for example, drying, rheology etc.

EMBODIMENTS

In order that the present invention may be more readily understood we provide the following non-limiting embodiments.

The formula for specific examples of dyes in accordance with the present invention are given below.

Examples of infrared dyes in accordance with the present invention are compounds 5-12 given below.



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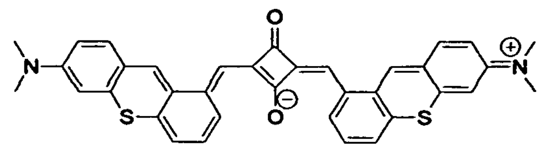

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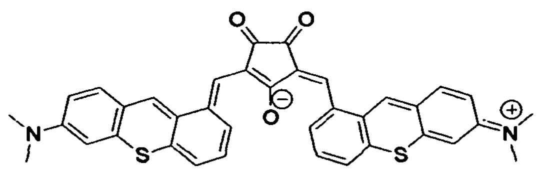

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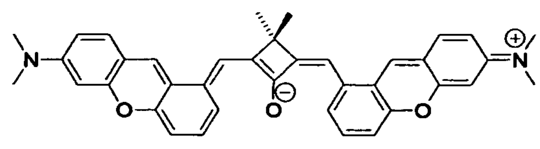

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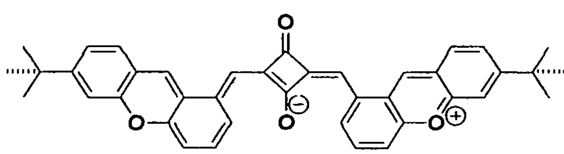

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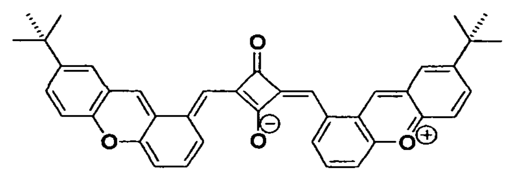

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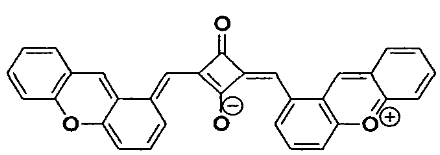

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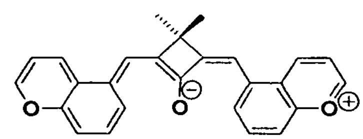

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The absorption spectra for compounds 5 to 12 were calculated and are given in Figures 1 to 8 respectively. As can be seen from the spectra, the compounds in accordance with the present invention have absorption peaks of at least about 950 nanometers and a high ratio of infrared absorption at the compound's peak position to the absorption in the visible region.

Throughout this specification the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the

specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

Dated this fourteenth day of August 2000

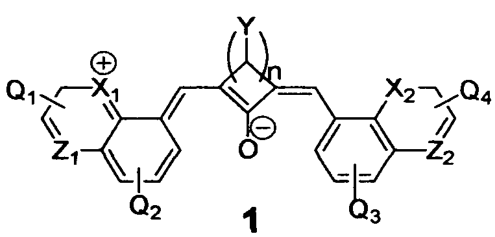
Silverbrook Research Pty Ltd

CLAIMS:

1. An infrared dye wherein the dye comprises two bridged diarylpolymethine type dyes or derivatives thereof connected together at either the 3, 4, 5 or 6 position by a central moiety such that the two dyes are located on each side of the central moiety, wherein the infrared dye absorbs strongly in the near infrared region of the spectrum but poorly in the visible region of the spectrum.

2. An infrared dye according to claim 1 wherein the central moiety is selected from the group consisting of squarylium, croconium, methinologs thereof and derivatives thereof.

3. An infrared dye of formula 1, 2, 3 or 4 as set out hereunder:



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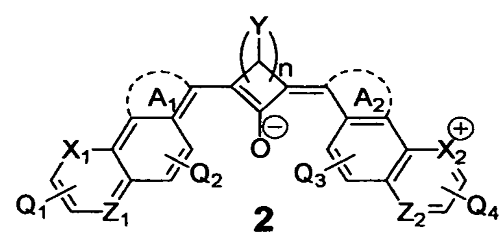

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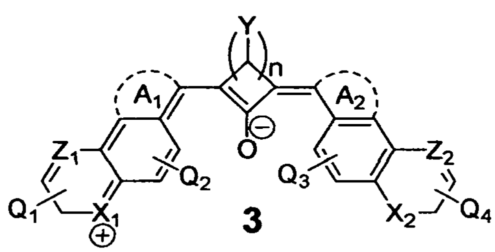

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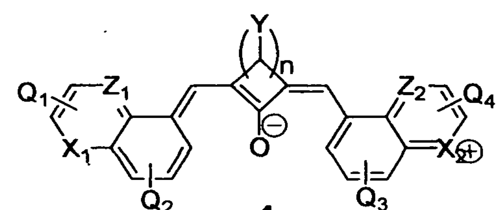

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wherein A_1 and A_2, taken individually, is/are absent or selected from the group consisting of a 5-membered polyene ring containing 0, 1 or 2 substituents that are selected from the group R;

X_1 and X_2 are individually selected from the group consisting of oxygen, sulfur, selenium, tellurium, CR_1R_2, NR_1, SiR_1R_2, GeR_1R_2, PR_1 where R_1 and R_2, which may the same or different, are selected from the group R;

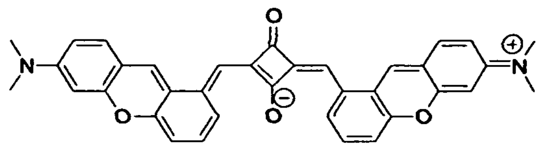
Z_1 and Z_2 are individually selected from CR_3 or N where R_3 is selected from the group R;

Q_1, Q_2, Q_3 and Q_4 are individually selected from the group consisting of R_4, a fused 6-membered aromatic ring optionally substituted with 1 to 4 substituents individually selected from R_5, and fused polyaromatic rings optionally substituted with one or more substituents selected from R_6 wherein R_4,, R_5 and R_6 are individually selected from the group R ;

R is the group consisting of hydrogen atom, a substituted or unsubstituted alkyl group, a substituted or unsubstituted aryl group, a substituted or unsubstituted aralkyl group, a halide atom, a hydroxy group, a substituted or unsubstituted amine group, a substituted or unsubstituted alkoxy group; and

n is 1 or 2 or 3.

4. An infrared dye according to claim 3 selected from:



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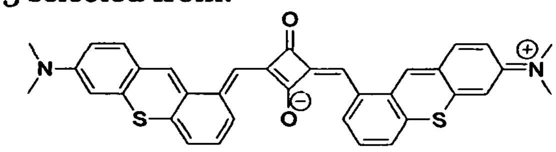

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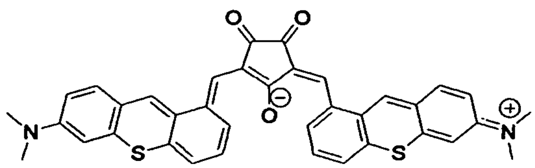

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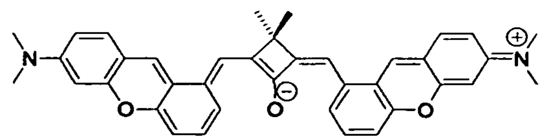

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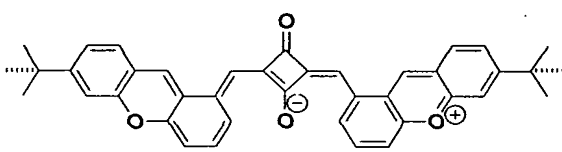

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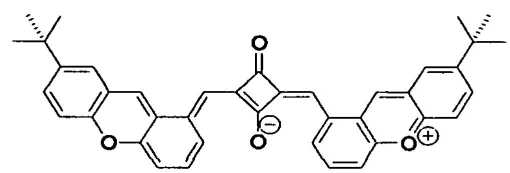

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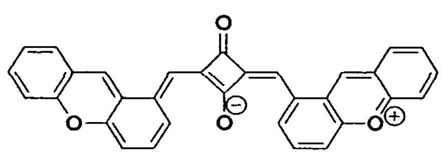

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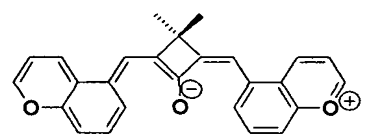

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5. An infrared printing ink comprising a colorant, wherein the colorant is a dye in accordance with claim 1 or claim 2.

6. An infrared printing ink according to claim 5 which is suitable for ink jet printing ink or offset printing.

ABSTRACT

An infrared dye, characterised in that the dye comprises two bridged diarylpolymethine type dyes or derivatives thereof connected together at either the 3, 4, 5 or 6 position by a central moiety such that the two dyes are located on each side of the central moiety, wherein the infrared dye absorbs strongly in the near infrared region of the spectrum but poorly in the visible region of the spectrum.

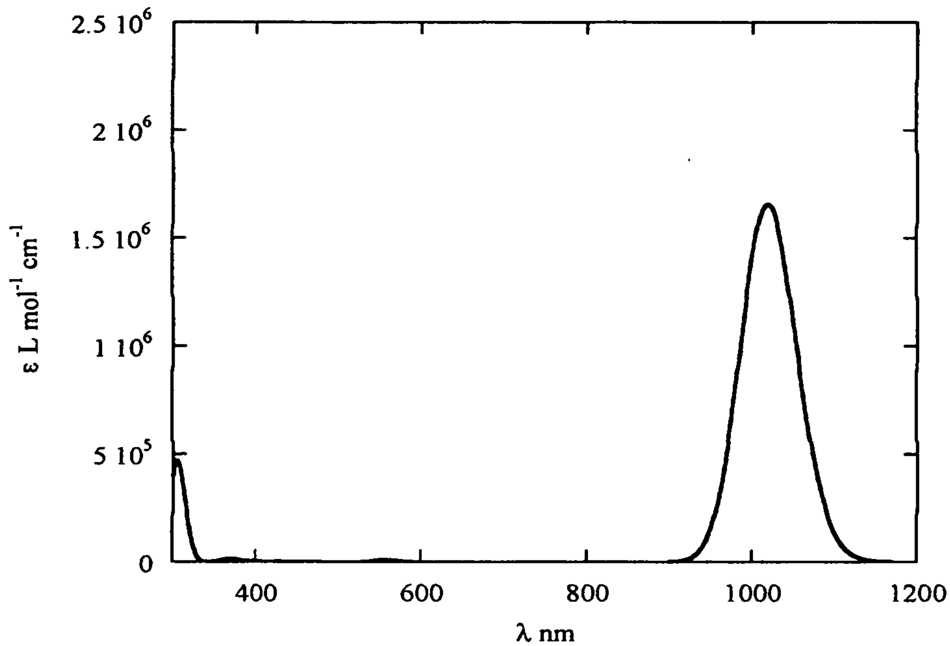

Figure 1: Calculated absorption spectra for **5**

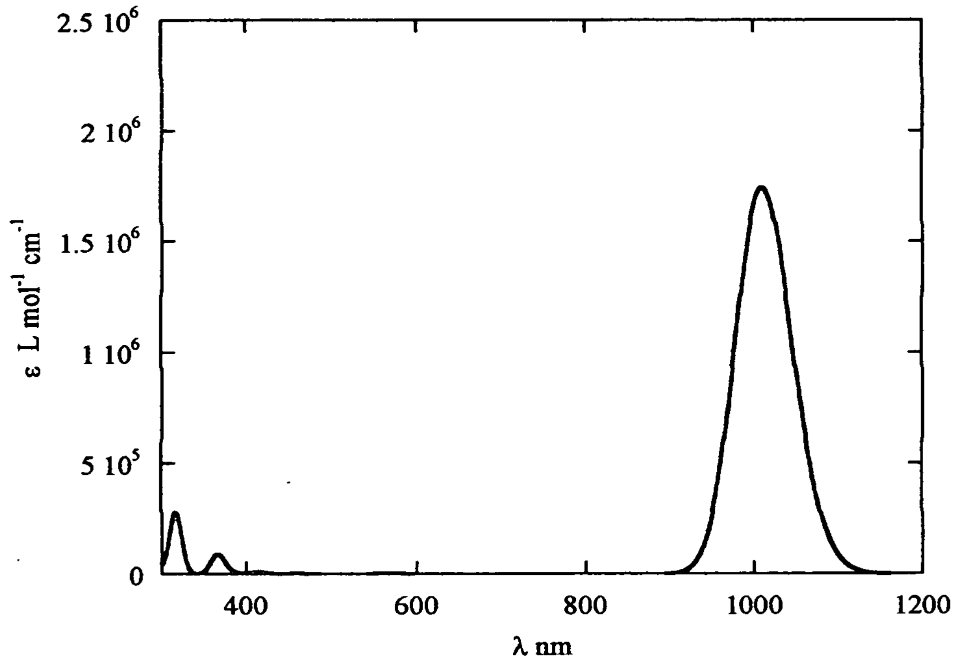

Figure 2: Calculated absorption spectra for **6**

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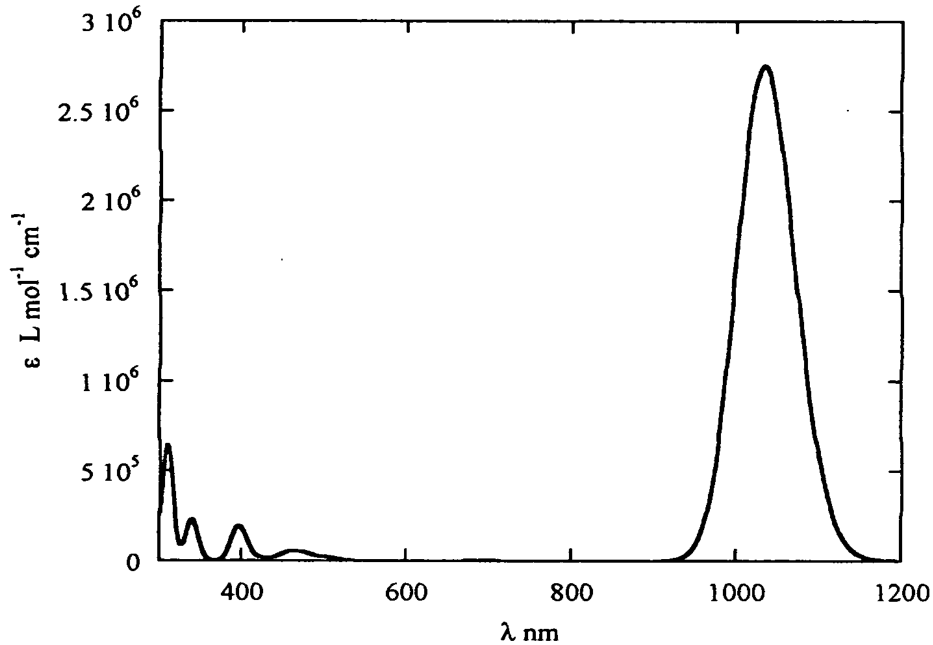

Figure 3: Calculated absorption spectra for 7

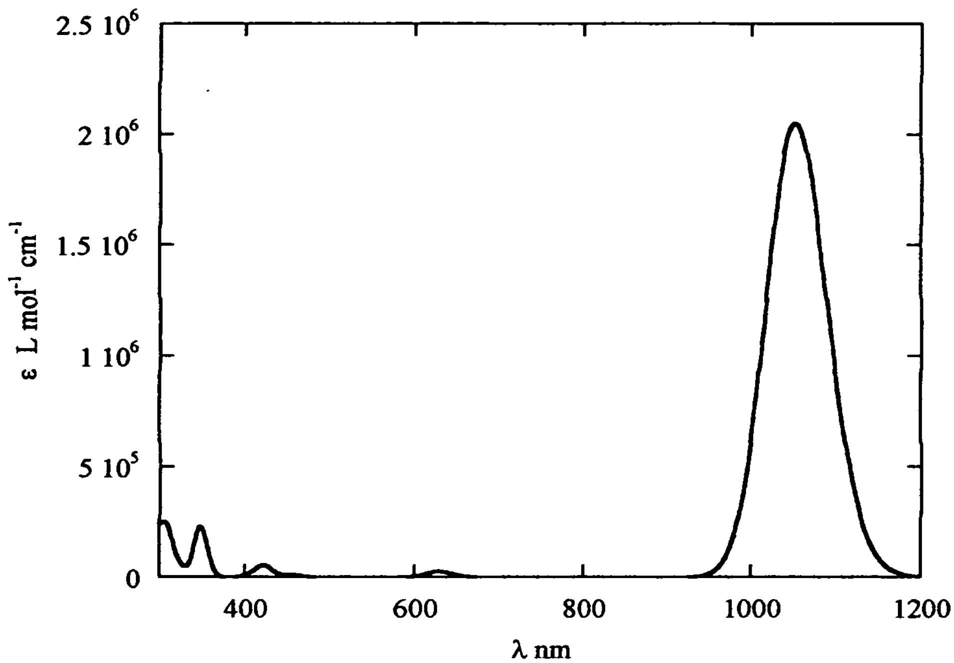

Figure 4: Calculated absorption spectra for **8**

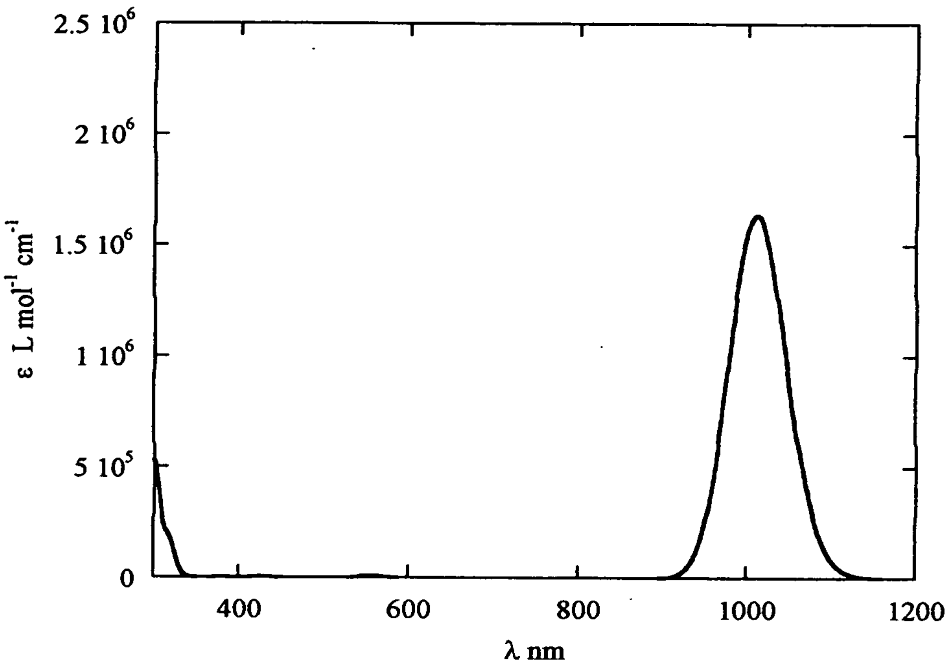

Figure 5: Calculated absorption spectra for **9**

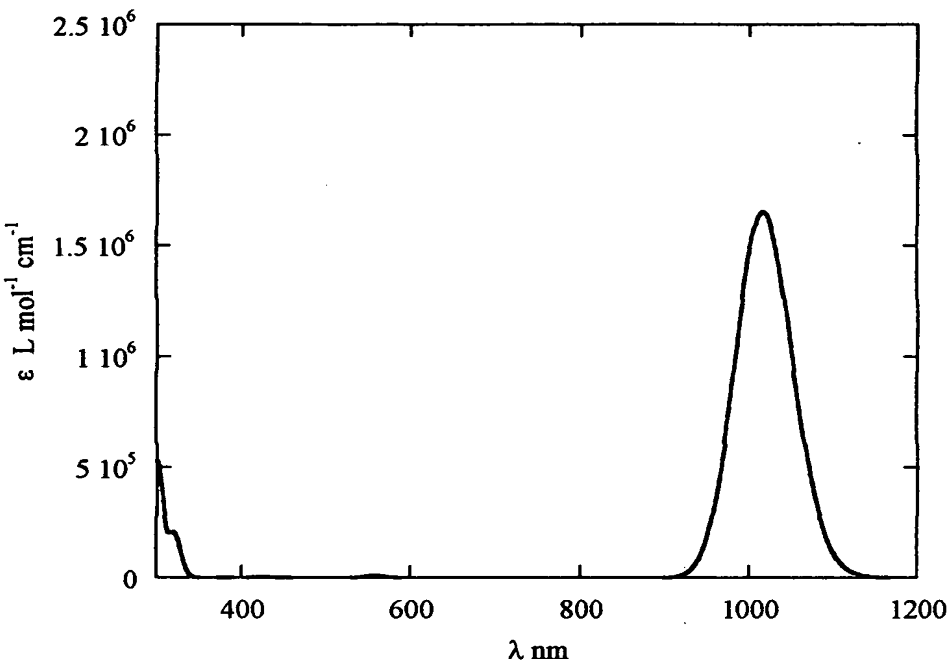

Figure 6: Calculated absorption spectra for **10**

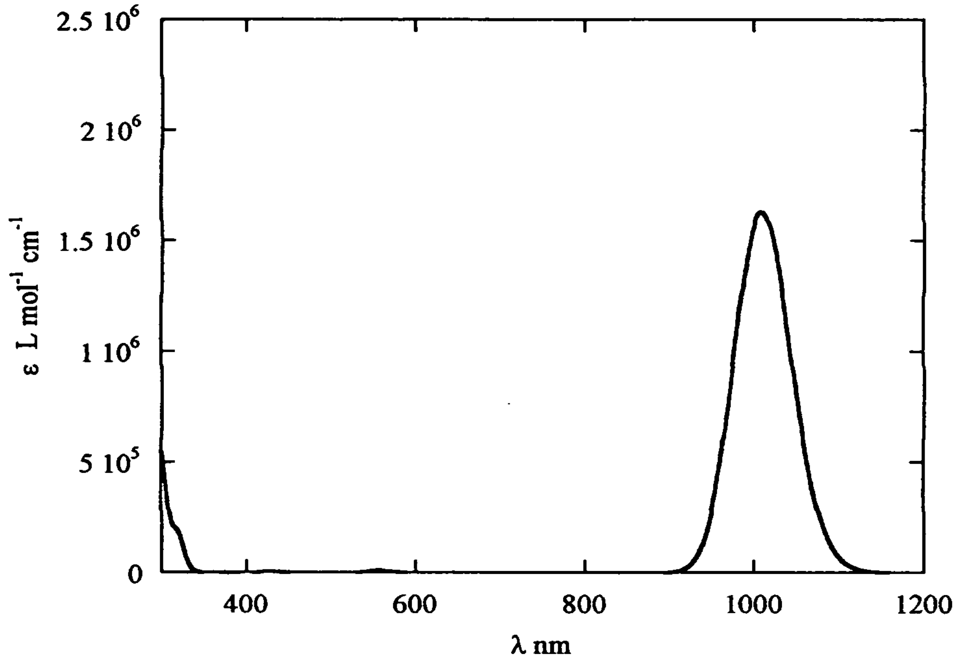

Figure 7: Calculated absorption spectra for **11**

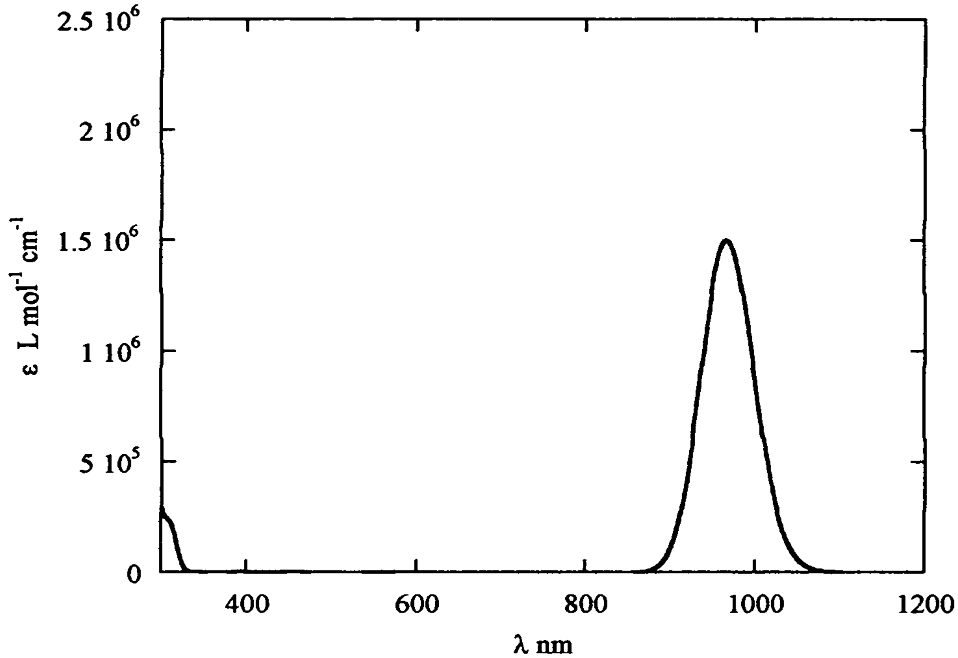

Figure 8: Calculated absorption spectra for 12